PATENT ABSTRACTS OF JAPAN

(11)Publication number : **10-182163**

(43)Date of publication of application : **07.07.1998**

(51)Int.Cl. C01G 49/08
C01G 51/00
G03G 9/083

(21)Application number : **08-356840**

(22)Date of filing : **25.12.1996**

(71)Applicant : **TODA KOGYO CORP**

(72)Inventor : **YOSHIZAWA MINORU**
AOKI ISATAKA
MISAWA HIROMITSU
MIYAZAKI SHIGENORI
UCHIDA NAOKI

(54) MAGNETIC IRON OXIDE PARTICLE, MAGNETIC IRON OXIDE PARTICLE POWDER CONSISTING MAINLY OF THE PARTICLE AND USED FOR MAGNETIC TONER AND MAGNETIC TONER USING THE MAGNETIC IRON OXIDE PARTICLE POWDER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain magnetic iron oxide particles capable of preventing their dropping from toner particles and imparting good fluidity and uniform antistaticity to the toner by specifying the particle diameter, Si content, particle shape and surface projection number of the magnetic particles.

SOLUTION: The magnetic iron oxide particles comprise magnetite particles, contains Si in an amount of 0.9-6.5atom% based on Fe, and has a particle diameter range of 0.05-0.50μm, a crenated shape based on a particulate shape and 2-30 projections on the surface of the particle on a projection chart. The surfaces of the particles are coated with either one of the oxide, hydroxide, hydrous oxide or their mixture of one or more kinds of elements selected from Al, Ti, Mg, Si, Co, Zr, Mn and Zn. The surfaces of the particles are preferably further coated with a hydrophobic treatment agent. When the particles are used for a toner, the particles are preferably used in a particle number rate of ≥60%.

LEGAL STATUS

[Date of request for examination] 13.03.2001

[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3578191
[Date of registration]	23.07.2004
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Particle diameter is 0.05-0.50 micrometers, and they are the magnetite particles which contain the silicon of 0.9 - 6.5 atom % to Fe by Si conversion. The particle shape has the shape of konpeito with the round angle based on the shape of a grain. On the particle front face aluminum, The oxide of a kind or two sorts or more of elements chosen from Ti, Mg, Si, Co, Zr, Mn, and Zn, The magnetic-oxide-of-iron particle which either a hydroxide, water oxides or such mixture have covered, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.

[Claim 2] The magnetic-oxide-of-iron particle which particle diameter is 0.05-0.50 micrometers, it is the magnetite particles which contain the silicon of 0.9 - 6.5 atom % to Fe by Si conversion, the particle shape has the shape of konpeito with the round angle based on the shape of a grain, and the hydrophobing processing agent has covered the particle front face, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.
[Claim 3] Particle diameter is 0.05-0.50 micrometers, and they are the magnetite particles which contain the silicon of 0.9 - 6.5 atom % to Fe by Si conversion. The particle shape has the shape of konpeito with the round angle based on the shape of a grain. On the particle front face aluminum, The oxide of a kind or two sorts or more of elements chosen from Ti, Mg, Si, Co, Zr, Mn, and Zn, The magnetic-oxide-of-iron particle which either a hydroxide, water oxides or such mixture have covered, and the hydrophobing processing agent has covered further, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.
[Claim 4] Magnetic-oxide-of-iron particle powder for magnetic toners characterized by including one of magnetic-oxide-of-iron particles according to claim 1 to 3 60% or more at a number rate in the magnetite-particles powder which mean particle diameter is 0.05-0.50 micrometers, and contains the silicon of 0.9 - 6.5 atom % to Fe by Si conversion.
[Claim 5] The magnetic toner using the magnetic-oxide-of-iron particle powder for magnetic toners according to claim 4.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention does not have omission from a toner particle, and relates to the magnetic toner which used this magnetic-oxide-of-iron particle powder for the magnetic-oxide-of-iron particle powder list for magnetic toners from which the image quality of high resolution is acquired in electrostatic latent-image development according to the fluidity when making it a toner being good.
[0002]
[Description of the Prior Art] The developing-negatives method by the so-called "one component system magnetism toner" using the complex particle which carried out mixed distribution of the magnetic particle powder, such as magnetite-particles powder, into binding resin as one of the electrostatic latent-image developing-negatives methods, without using a carrier as a developer is learned widely, and is used widely.
[0003] Recently, the magnetic toner excellent in the endurance from which the improvement in a property of the magnetic toner which is a developer, i.e., the development engine performance stabilized also on the hard service condition, is obtained is strongly demanded with high-performance-izing of the miniaturization of an electrostatic-process-copying-machine machine and a printing machine machine, improvement in the speed, etc. Moreover, the magnetic toner from which high resolution is obtained according to a fluidity being high is called for.
[0004] Usually, a magnetic toner consists of a magnetic particle and binding resin, and the magnetic particle is distributed by homogeneity in the toner particle. The magnetic particle exposed to a toner particle front face tended to drop out of a toner particle by friction etc., the rate of the magnetic particle especially exposed to a front face in the diameter toner of a granule increased, pulverization of the magnetic particle which drops out of a toner particle front face carried out, it worsens the environment in a device, or the omissive magnetic particle powder disperses at the time of electrostatic development it not only bars uniform electrification of a toner, but, and the problem of reducing development nature has produced it. Then, dedropping is called on for the magnetic particle powder excellent in pile endurance even if it exposes to a toner particle front face.
[0005] the resolution at the time of electrostatic latent-image development -- the inside of JP,63-139367,A -- "-- a developer having a high fluidity in the approach of using such a dry-developing agent, in order to form the visible image of good image quality, and having uniform electrification nature -- required ... " -- the fluidity of a toner particle and homogeneity electrification nature which are a developer are involving greatly as it is a publication. For this reason, the toner which has a high fluidity in order to obtain the image of high resolution, and has uniform electrification nature is called for.
[0006] There is relation with many close properties of the magnetic particle powder by which mixed distribution is carried out into many properties of a magnetic toner and a magnetic toner, and it depends for the fluidity of a magnetic toner on the surface state of the magnetic particle exposed to a magnetic toner particle front face greatly. Then, it is known as given in JP,7-101731,A etc. at JP,5-72801,A and a JP,5-213620,A list that it is effective in using the magnetic particle powder which has Si for a front face

raising the fluidity of a magnetic toner.
[0007] It is required that a magnetic toner should be exposed to an elevated temperature 150 degrees C or more on the occasion of use, and its color tone should be stable also in this case. This fact is JP,55-65406,A. "generally many following properties are required of the magnetic powder for magnetic toners in such 1 component method. ... Have the blackness which is equal to iv practical use. Although a coloring agent can also be made to contain in a magnetic toner, it is more desirable for the fine particles itself to have black and not to use a coloring agent. v) Thermal resistance is high. A stable enough thing is required in the temperature requirement a color tone especially blackness, and whose electromagnetic characteristic are about 0-150 degrees C. ... It is as an unstated publication."
[0008] It originates in Fe2in magnetite particles+ oxidizing, if 150 degrees C is especially exposed to an about 200-degree C elevated temperature, although it is in the inclination for whenever [black] to be excellent, so that whenever [of magnetite particles / black] depends on the content of Fe2+ for the phenomenon in which a color tone changes to blackish brown from black, as everyone knows and there are many Fe2+ contents, and becoming Fe3+, and metamorphosing into maghemite.
[0009] Moreover, when a particle front face is generally a hydrophilic property, the distribution to resin becomes difficult, magnetic particle powder becomes uneven [the content of a magnetic particle] between magnetic toner particles, consequently condensation magnetic as a core becomes easy to occur a magnetic toner particle with many contents of a magnetic particle. This brings the result that the oil absorption of magnetic particle powder increases, and appears. Then, in order to obtain the magnetic toner in which high resolution is possible, in order to improve the dispersibility to the resin of magnetic particle powder, the particle front face of magnetic particle powder is hydrophobicity, and it is required that there is little oil absorption.
[0010] The magnetite-particles powder (JP,44-668,B) with which the magnetite-particles powder used as magnetic particle powder for magnetic toners presented octahedron, the magnetite particles (JP,62-51208,B) which presented the shape of a ball, the magnetite particles (JP,3-201509,A) which presented hexahedron further, etc. are known.
[0011] Moreover, there are magnetite particles (JP,5-345616,A) which have a granular projection in a particle front face as a thing of characteristic particle shape, magnetite particles (JP,5-43253,A) with which the number of pages of a front face has at least ten or more polyhedrons.
[0012] Examination of the manufacturing method which adds Si during a magnetite generation reaction for the property improvement of magnetite particles is performed conventionally. For example, after adding a silicon component in a ferrous-salt solution and mixing with 1.0-1.1Eq alkali to iron, Oxidize by maintaining pH to 7-10, and the insufficient iron which becomes 0.9-1.2Eq to the alkali original in the middle of a reaction is added. How (JP,5-213620,A) to obtain magnetite particles by oxidizing by maintaining to pH 6-10, In making magnetite particles generate by carrying out aeration of the oxygen content gas to the ferrous-salt reaction water solution containing the ferrous hydroxide colloid which 0.80-0.99Eq hydroxylation alkali was made to react to Fe2+, and was obtained 0.1-5.0 atom % addition of a water-soluble silicate is done by Si conversion to Fe. How (JP,3-9045,B) to obtain the magnetite-particles powder which presented the ball type by carrying out 2 staircase reactions, The alkali water solution more than the equivalent is added in a ferrous-salt solution. During the oxidation reaction to the magnetite particles after ferrous hydroxide generation To the stage whose Fe2+/Fe3+ ratios in a reaction solution are 10-1.0 about a hydroxo silicate solution, it is Si/Fe 3O4. There is a manufacturing method (JP,1-36864,B) of the magnetite pigment added at 0.5 - 3.0% of the weight of a rate by the ratio etc.
[0013] Moreover, in order to reduce oil absorption by carrying out hydrophobing of the approach (JP,8-133745,A) and particle front face which form the enveloping layer which benefits a heat-resistant improvement from hydroxides, such as Si, aluminum, and Ti, and a water oxide, there is the approach (JP,7-277738,A) of carrying out hydrophobing processing by hydrophobing processing agents, such as a coupling agent, silicone, and a higher fatty acid, etc.
[0014]
[Problem(s) to be Solved by the Invention] There are no omission from a toner particle, and although the magnetic-oxide-of-iron particle powder for magnetic toners with which the image quality of high

resolution is acquired in electrostatic latent-image development is just going to be demanded most now since electrification nature with it is obtained, such magnetic-oxide-of-iron particle powder for magnetic toners is not yet offered. [the good fluidity when making it a toner and] [uniform]
[0015] namely, the above -- although magnetite-particles powder given in JP,5-345616,A has a granular projection on a particle front face, each projection is detailed and it is inferior to the effectiveness of sufficient omission prevention in it.
[0016] the above -- although magnetite-particles powder given in JP,5-43253,A consists of a particle which has ten or more fields, since it does not have irregularity, it does not have the omission prevention effectiveness from a toner front face.
[0017] the above -- magnetite particles given in JP,5-213620,A have added 1.0-1.1Eq alkali to the first iron in first order reaction, the magnetite particles obtained are close to a globular form, and the thing of particle diameter with them is not obtained. [large particle size distribution and] [uniform]
[0018] the above -- magnetite particles given in JP,3-9045,B do not have pH adjustment at the time of first order reaction, pH is as low as less than 8.0, and a configuration is a globular form thing.
[0019] the above -- a configuration is an octahedron-like thing, and since magnetite particles given in JP,1-36864,B do not have irregularity, they do not have the omission prevention effectiveness from a toner front face.
[0020] Then, this invention does not have omission from a toner particle, and since electrification nature with it is obtained, it makes it a technical technical problem to offer the magnetic toner using the magnetic-oxide-of-iron particle powder for magnetic toners and this magnetic-oxide-of-iron particle powder with which the image quality of high resolution is acquired in electrostatic latent-image development. [the good fluidity when making it a toner and] [uniform]
[0021]
[Means for Solving the Problem] This invention as follows can attain said technical technical problem.
[0022] Namely, this invention is magnetite particles with which particle diameter is 0.05-0.50 micrometers, and contains the silicon of 0.9 - 6.5 atom % to Fe by Si conversion. The particle shape has the shape of konpeito with the round angle based on the shape of a grain. On the particle front face aluminum, The oxide of a kind or two sorts or more of elements chosen from Ti, Mg, Si, Co, Zr, Mn, and Zn, It is the magnetic-oxide-of-iron particle which either a hydroxide, water oxides or such mixture have covered, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.
[0023] Moreover, particle diameter is 0.05-0.50 micrometers, it is the magnetite particles which contain the silicon of 0.9 - 6.5 atom % to Fe by Si conversion, the particle shape has the shape of konpeito with the round angle based on the shape of a grain, and this invention is a magnetic-oxide-of-iron particle which the hydrophobing processing agent has covered the particle front face, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.
[0024] Moreover, this invention is magnetite particles with which particle diameter is 0.05-0.50 micrometers, and contains the silicon of 0.9 - 6.5 atom % to Fe by Si conversion. The particle shape has the shape of konpeito with the round angle based on the shape of a grain. On the particle front face aluminum, The oxide of a kind or two sorts or more of elements chosen from Ti, Mg, Si, Co, Zr, Mn, and Zn, It is the magnetic-oxide-of-iron particle which either a hydroxide, water oxides or such mixture have covered, and the hydrophobing processing agent has covered further, and is characterized by the number of the convex projections on a particle front face being 2-30 range on projection drawing.
[0025] Moreover, mean particle diameter is 0.05-0.50 micrometers, and this invention is magnetic-oxide-of-iron particle powder for magnetic toners characterized by including either of said magnetic-oxide-of-iron particles 60% or more at a number rate in the magnetite-particles powder which contains the silicon of 0.9 - 6.5 atom % to Fe by Si conversion.
[0026] Moreover, this invention is the magnetic toner which used said magnetic-oxide-of-iron particle powder for magnetic toners.
[0027] It will be as follows if the configuration of this invention is explained in more detail. First, the magnetic-oxide-of-iron particle concerning this invention is described.

[0028] The magnetic-oxide-of-iron particle concerning this invention may consist of magnetite particles (FeO) (x-Fe 2O3, 0< x<=1) in presentation, and may be included below 10 atom % to Fe by making into a total amount a kind or two sorts or more of metallic elements which are metallic elements other than iron and are chosen from Mn, Zn, nickel, Cu, aluminum, and Ti.
[0029] the magnetic-oxide-of-iron particle concerning this invention -- Si -- Fe -- receiving -- 0.9 to 6.5 atom % -- it is made desirable 1.3-5.3 atom % content.
[0030] 0.05-0.50 micrometers of particle diameter of the magnetic-oxide-of-iron particle concerning this invention are 0.10-0.30 micrometers preferably.
[0031] The magnetic-oxide-of-iron particle concerning this invention is a particle of the shape of konpeito with the round angle based on the shape of a grain, and has preferably 2-30 particle surface convex-like projections [5-20] on projection drawing. In the case of the globular shape by which particle shape is known well conventionally, octahedron, hexahedron, or a polyhedron, when it exposes to a toner particle front face, it is easy to drop out. When the number of said projections is less than two, the effectiveness of the omission prevention from a toner particle front face becomes few things. When exceeding 30 pieces, although the contact part with resin increases in a toner particle front face, each projection becomes small and the effectiveness of sufficient omission prevention is not acquired.
[0032] The convex projection in this invention fulfills the following conditions. That is, both the both ends of (1) projection should be concaves on the projection drawing (transmission electron microscope photograph etc.) of a magnetic-oxide-of-iron particle.
(2) When two or more steps of projection parts have lapped, let only a part for the point be a projection.
(3) Satisfy the following type about the die length (a) of the base of a projection, height (b), and the particle diameter (c) of the particle concerned.
i) 10 <=a/cx100 <=40ii5 <=b/cx100 <=30[0033] The above (1) and (2) are judged by viewing on said projection drawing (transmission electron microscope photograph etc.). It judges whether a/c and b/c are computed by measuring [each / of the projection which is about the above (3) on the particle front face of the magnetic-oxide-of-iron particle in said projection drawing (transmission electron microscope photograph etc.)] about the die length (a) of a base, height (b), and the particle diameter (c) of the particle concerned, and Conditions i and ii are suited.
[0034] In addition, drawing 1 is the conceptual explanatory view in which having expanded the gestalt of the magnetic-oxide-of-iron particle which fulfills the conditions of aforementioned (1) - (3), and having shown it in model. "Both both ends are concaves" in the above (1) points out the part shown by the arrow head A, only the amount of [in the above (2) / "the amount of"] point points out the part shown by the arrow head B, and "the die length (a), the height (b), and the particle diameter (c)" in the above (3) are a, b, and c in this drawing.
[0035] aluminum, Ti, Mg, Si, Co, Zr and Mn on the front face of a particle of the magnetic-oxide-of-iron particle which either the oxide of a kind or two sorts or more of elements (henceforth "a specific element") chosen from aluminum, Ti, Mg, Si, Co, Zr, Mn, and Zn, a hydroxide, water oxides or such mixture have put on the particle front face concerning this invention, and the amount of Zn covering are 0.02 - 10 % of the weight preferably.
[0036] It is desirable that a kind or two sorts or more of hydrophobing processing agents chosen from a coupling agent, silicone, and a higher fatty acid have covered the particle front face of the magnetic-oxide-of-iron particle which the hydrophobing processing agent has put on the particle front face concerning this invention.
[0037] As said coupling agent, a silane coupling agent, a titanate coupling agent, an aluminates coupling agent, etc. can be used. Silicone oil etc. can be used as said silicone. As said higher fatty acid, stearin acid, isostearic acid, a palmitic acid, an iso palmitic acid, oleic acid, etc. can be used.
[0038] The amount of covering of said hydrophobing processing agent is 0.2 - 5.0 % of the weight more preferably 0.1 to 10.0% of the weight.
[0039] The amount of covering of said specific element on the front face of a particle of the magnetic-oxide-of-iron particle which either the oxide of said specific element, a hydroxide, water oxides or such mixture have put on the particle front face concerning this invention, and the hydrophobing processing

agent has put further is 0.02 - 10 % of the weight preferably. Furthermore, the amount of covering of said hydrophobing processing agent is 0.2 - 5.0 % of the weight more preferably 0.1 to 10.0% of the weight.
[0040] Next, the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention is described.
[0041] The magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention It consists of magnetite particles (FeO) (x, Fe 2O3, 0< x<=1) in presentation. It is the konpeito configuration where the angle based on the shape of a grain is round, and is the particle powder which contains preferably the magnetic-oxide-of-iron particle which has 2-30 convex projections on this particle front face 70% or more 60% or more at a number rate as shown in the electron microscope photograph of the post- release of drawing 2 . When the number percentage is less than 60%, and it considers as a toner, the effectiveness of the omission prevention from a toner particle front face becomes few things. In addition, a convex projection means what fulfills the above (1) thru/or the conditions of (3) here.
[0042] Said number rate measured the number of a magnetic-oxide-of-iron particle which satisfies the above (1) thru/or the conditions of (3) in a transmission electron microscope photograph, and computed it as a rate of occupying to the total particle number which measured. In addition, as a total of the particle which measures at this time, 30 or more pieces are preferably made into 50 or more pieces.
[0043] 0.05-0.50 micrometers of mean particle diameter of the magnetic toner magnetic-oxide-of-iron particle powder concerning this invention are 0.10-0.30 micrometers preferably. When mean particle diameter is less than 0.05 micrometers, in order that the particle in the unit volume may increase too much and the number of contacts between particles may increase, when the adhesion force between powder beds becomes large and considers as a magnetic toner, the dispersibility to the inside of binding resin worsens. When exceeding 0.50 micrometers, the number of the magnetic-oxide-of-iron particle contained in the toner particle of a piece decreases, and a bias arises in distribution of a magnetic-oxide-of-iron particle about each toner particle, consequently the homogeneity of electrification of a toner is spoiled.
[0044] the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention -- a BET specific surface area -- 3-30m2 / g -- they are 5-20m2 / g preferably.
[0045] The saturation magnetization value of the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention is the range of 82 - 90 emu/g preferably 80 to 92 emu/g. The value of 92 emu/g is a theoretical value of magnetite, and when exceeding this, there is. [no] Since in the case of less than 80 emu/g the red taste is worn in order that the amount of Fe2+ in a particle may decrease, it is not desirable as magnetic-oxide-of-iron particle powder for magnetic toners.
[0046] The Fe2+ content of the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention is 17 - 24 % of the weight preferably 12 to 24% of the weight to magnetic-oxide-of-iron particle all weight. Whenever [for less than 12% of the weight of a case / sufficient / black] is not obtained. it oxidizes, in exceeding 24 % of the weight -- having -- easy -- an environment -- it will become unstable.
[0047] the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention -- Si -- Fe -- receiving -- 0.9 to 6.5 atom % -- it is made desirable 1.3-5.3 atom % content. When the content of Si is under 0.9 atom %, since Si contained on a front face decreases, it is inferior to a fluidity. Since the amount of Si to contain increases in more than 6.5 atom %, when hygroscopicity becomes high and considers as a toner, the environmental stability of a toner may be affected. Moreover, Si which exists independently apart from magnetic-oxide-of-iron particle powder checks uniform electrification, and may degrade electrification stability. moreover, Si content on said front face of a particle -- Fe -- receiving -- 0.05 to 1.0 atom % -- it is 0.08 to 0.80 atom % preferably. When it considers as a toner, a good fluidity is not acquired at the case of under 0.05 atom %. In exceeding 1.0 atom %, hygroscopicity becomes high, and when it considers as a toner, the environmental stability of a toner may be affected.
[0048] aluminum, Ti, Mg, Si, Co, Zr and Mn on the front face of a particle of the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which either

the oxide of a specific element, a hydroxide, water oxides or such mixture have put on the particle front face concerning this invention 60% or more at a number rate, and the amount of Zn covering are 0.02 - 10 % of the weight preferably. Sufficient thermal resistance for less than 0.02% of the weight of a case is not obtained. When exceeding 10 % of the weight, since all Si that exists in a particle front face is covered and a fluidity falls, it is not desirable.

[0049] It is desirable that a kind or two sorts or more of hydrophobing processing agents chosen from a coupling agent, silicone, and a higher fatty acid have covered the particle front face of the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which the hydrophobing processing agent has put on the particle front face concerning this invention 60% or more at a number rate.

[0050] The amount of covering of said hydrophobing processing agent is 0.2 - 5.0 % of the weight more preferably 0.1 to 10.0% of the weight. Hydrophobicity is not enough for less than 0.1% of the weight of a case. When exceeding 10.0 % of the weight, since all Si on the front face of a particle is covered and a fluidity falls, it is not desirable.

[0051] The amount of covering of said specific element on the front face of a particle of the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which either the oxide of said specific element, a hydroxide, water oxides or such mixture have put on the particle front face concerning this invention, and the hydrophobing processing agent has put further 60% or more at a number rate is 0.02 - 10 % of the weight preferably. Sufficient thermal resistance for less than 0.02% of the weight of a case is not obtained. When exceeding 10 % of the weight, since all Si that exists in a particle front face is covered and a fluidity falls, it is not desirable. Furthermore, the amount of covering of said hydrophobing processing agent is 0.2 - 5.0 % of the weight more preferably 0.1 to 10.0% of the weight. Hydrophobicity is not enough for less than 0.1% of the weight of a case. When exceeding 10.0 % of the weight, since all Si on the front face of a particle is covered and a fluidity falls, it is not desirable.

[0052] The condensation which is a fluid characteristic is 45 or less preferably, and the fluidity of condensation of the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention is [50 or less] good.

[0053] the magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention -- the amount of electrifications -- +20 - -60microC/g -- they are +10 - -50microC/g preferably.

[0054] the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which the hydrophobing processing agent has put on the particle front face concerning this invention 60% or more at a number rate -- desirable -- oil absorption -- 20ml/-- 100g or less is 18ml / 100g or less more preferably.

[0055] The magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which either the oxide of said specific element, a hydroxide, water oxides or such mixture have put on the particle front face concerning this invention 60% or more at a number rate is desirable, and exoergic initiation temperature is 150 degrees C or more.

[0056] Next, the manufacturing method of said magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention as aforementioned is described.

[0057] As a ferrous-salt water solution in the first stage reaction of this invention, there are a ferrous-sulfate water solution, a ferrous chloride water solution, etc.

[0058] As a hydroxylation alkali water solution in the first stage reaction of this invention, a carbonic acid alkali water solution, aqueous ammonia, etc., such as a water solution of the hydroxide of alkaline earth metal, such as a water solution of the hydroxide of alkali metal, such as a sodium hydroxide and a potassium hydroxide, a magnesium hydroxide, and a calcium hydroxide, and a sodium carbonate, potassium carbonate, and an ammonium carbonate, can be used.

[0059] The amount of the hydroxylation alkali water solution used before pH adjustment in said first stage reaction is 0.80-0.99Eq to Fe2+ in a ferrous-salt water solution. It is the range of 0.90-0.99Eq preferably. In the case of less than 0.80Eq, goethite cannot mix into a product and the target magnetite particles cannot be obtained as a single phase. When exceeding 0.99Eq, particle size distribution become

large and the thing of uniform particle diameter is not obtained.
[0060] The reaction temperature in the first stage reaction of this invention is 70-100 degrees C. In being less than 70 degrees C, it intermingles a needle shape crystal goethite particle. Also when exceeding 100 degrees C, although they are generated, since magnetite particles need equipments, such as an autoclave, they are not industrially easy.
[0061] The oxidation means in the first stage reaction of this invention is performed by carrying out aeration of the oxygen content gas (for example, air) into liquid.
[0062] A sodium silicate, a potassium silicate, etc. can be used as a water-soluble silicate used in the first stage reaction of this invention. the addition of said water-soluble silicate -- Fe -- receiving -- Si conversion -- 1.0 to 8.0 atom % -- it is 1.5 to 6.5 atom % preferably. It becomes a hexahedron particle at the case of under 1.0 atom %, and is inferior to the effectiveness of the omission prevention from a toner front face. On the other hand, in exceeding 8.0 atom %, it intermingles a needlelike goethite particle. Moreover, since the amount of the silicon to contain increases, when the amount of adsorption moisture increases and it considers as a toner, the environmental stability of a toner may be affected. Moreover, Si which deposits independently apart from magnetic-oxide-of-iron particle powder checks uniform electrification, and is inferior to electrification stability.
[0063] The addition stage of the water-soluble silicate in said first stage reaction carries out aeration of the oxygen content gas into the ferrous-salt reaction water solution which contains ferrous hydroxide colloid in the middle of a first stage reaction, and needs to be a process in the middle of a magnetite nucleus crystallite child's generation to it. The addition approach can be performed by dividing into 5 times or more, and adding, or being preferably, dropped at a continuation target twice or more. The dropping rate in the case of being dropped continuously is per minute 1.0 - 3.0% preferably per minute 0.5 to 5.0% to the total addition of a water-soluble silicate. When package addition is carried out, since it is hard to contain Si to the magnetic-oxide-of-iron particle to generate and deposits independently, it is not desirable.
[0064] the first stage reaction of this invention -- setting -- whenever [oxidation / of first iron Fe2+] -- (Fe3+ / total Fe) 20% or more of range -- setting -- pH of suspension -- the range of 7.5-9.5 -- whenever [said oxidation] (Fe3+ / total Fe) makes pH of suspension further the range of 8.0-9.5 in 30% or more of range. When there is no pH of suspension in this range, alkali, such as acids, such as a sulfuric acid, or a hydroxylation alkali water solution, adjusts pH of suspension in the range of 7.5-9.5. When Suspension pH is less than 7.5, irregularity decreases on a particle front face, it will become near spherically, and the effectiveness of the omission prevention from a toner front face is not enough. Si becomes being hard to contain on a particle front face, when Suspension pH exceeds 9.5, and when it considers as a toner, it becomes a thing inferior to a fluidity.
[0065] The amount of the hydroxylation alkali water solution used in the second stage reaction of this invention is 1.00Eq or more to Fe2+ at the time of second stage reaction initiation which remains. In less than 1.00Eq, Fe2+ which remains does not carry out whole-quantity precipitate. Practically, the amount in consideration of industry nature 1.00Eq or more is desirable.
[0066] The reaction temperature in the second stage reaction of this invention can be chosen from the same conditions as a first stage reaction, and can be performed. Moreover, an oxidation means can also be chosen from the same conditions as a first stage reaction, and can be performed.
[0067] In addition, sufficient stirring may be performed over necessary time amount as occasion demands between first stage reactions and between a first stage reaction and a second stage reaction the raw material addition back.
[0068] the specific element (aluminum and Ti --) on the front face of a particle of the magnetic-oxide-of-iron particle in this invention Covering of either the oxide of a kind or two sorts or more of elements chosen from Mg, Si, Co, Zr, Mn, and Zn, a hydroxide, water oxides or such mixture The inorganic compound of said selected element or its water solution can be added in the water suspension of magnetic-oxide-of-iron particle powder, or the water suspension after said second stage reaction termination, and it can carry out by adjusting pH to well-known pH field to which said specific element precipitates as an oxide, a hydroxide, and a water oxide.

[0069] To use the once dried magnetic-oxide-of-iron particle powder as water suspension of said magnetic-oxide-of-iron particle powder, it is required in order to obtain an enveloping layer with more uniform considering as the fully distributed water suspension. When using the water suspension of the magnetic-oxide-of-iron particle powder after second stage reaction termination as it is, since the above-mentioned distributed process is not needed, it is more industrial.
[0070] As an inorganic compound of said selected element, what is necessary is just a water-soluble thing. As an aluminum compound, an aluminum sulfate, an aluminum chloride, an aluminium nitrate, a sodium aluminate, etc. can be used. Sulfuric-acid titanyl, a titanium chloride, etc. can be used as a Ti compound. Magnesium sulfate, a magnesium chloride, etc. can be used as a Mg compound. As an Si compound, No. 3 water glass, a sodium silicate, a potassium silicate, etc. can be used. Cobalt sulfate, a cobalt chloride, etc. can be used as a Co compound. A sulfuric-acid zirconium, a zirconium chloride, etc. can be used as a Zr compound. A manganese sulfate, a manganese chloride, etc. can be used as a Mn compound. A zinc sulfate, a zinc chloride, etc. can be used as a Zn compound.
[0071] The addition of the inorganic compound of said selected element is 0.02 - 10 % of the weight preferably. Sufficient thermal resistance for less than 0.02% of the weight of a case is not obtained. When exceeding 10 % of the weight, other than a particle front face, it may deposit independently and is not desirable.
[0072] In the case of aluminum, it is the range of pH 4-12, and in the case of Ti, the preparation pH after adding the inorganic compound of said selected element is three or more pH, in the case of Mg, is 9.5 or more pH, in the case of Si, is 9.5 or less pH, in Co, is 7.5 or more pH, in the case of Zr, is two or more pH, in the case of Mn, is 8.5 or more pH, and, in the case of Zn, is the range of pH 6.5-14.
[0073] Although which approach of dry type processing or a wet process may be used for covering of the hydrophobing processing agent in this invention, it is good to carry out by dry type processing preferably, and can use a wheel mold kneading machine, a stone milling machine, a Henschel mixer, etc. in this case.
[0074] The addition of a hydrophobing processing agent is 0.2 - 5.0 % of the weight more preferably 0.1 to 10.0% of the weight. The effectiveness of hydrophobing is not enough, when exceeding 10.0 % of the weight, the whole quantity of a hydrophobing agent will not be put on a particle front face, but a hydrophobing agent will exist in less than 0.1% of the weight of a case independently, and it is not desirable.
[0075] The magnetic toner concerning this invention is described.
[0076] 3-20 micrometers of volume mean particle diameter of the magnetic toner concerning this invention are 5-15 micrometers preferably.
[0077] The magnetic toner concerning this invention may consist of said magnetic-oxide-of-iron particle powder for magnetic toners, and binding resin, and may contain a release agent, a coloring agent, an electric charge control agent, other additives, etc. if needed. the rate of said binding resin and said magnetic-oxide-of-iron particle powder for magnetic toners -- said binding resin 100 weight section -- receiving -- said magnetic-oxide-of-iron particle powder 20 - the 150 weight sections -- it is the 30 - 120 weight section preferably.
[0078] The magnetic toner concerning this invention does not almost have omission of the magnetic-oxide-of-iron particle from a toner front face.
[0079] The image quality of high resolution is acquired according to the magnetic toner concerning this invention having a good fluidity.
[0080] As binding resin used for said magnetic toner, a polymerization or the copolymerized vinyl system polymer can use vinyl system monomers, such as styrene, acrylic-acid alkyl ester, and alkyl methacrylate ester. As styrene of the monomer which constitutes this binding resin, for example, styrene, There are styrene, such as alpha methyl styrene and p-KURORU styrene, and a substitution product of those. As acrylic-acid alkyl ester For example, an acrylic acid, a methyl acrylate, an ethyl acrylate, butyl acrylate, There are acrylic-acid dodecyl, acrylic-acid octyl, isobutyl acrylate, and acrylic-acid hexyl. As alkyl methacrylate ester For example, the monocarboxylic acid which has double bonds, such as a methyl methacrylate, ethyl methacrylate, methacrylic-acid butyl, methacrylic-acid octyl,

methacrylic-acid isobutyl, methacrylic-acid dodecyl, and methacrylic-acid hexyl, its substitution product, etc. exist. It is desirable that a styrene system component is included in said copolymer 50 to 95% of the weight.

[0081] Well-known polymerization methods, such as a bulk polymerization, solution polymerization, a suspension polymerization, and an emulsion polymerization, are used for manufacture of said copolymer. Moreover, a well-known polymer or well-known copolymers, such as polyester system resin, epoxy system resin, and polyurethane system resin, can be used for binding resin if needed besides such a component.

[0082] As a release agent, with a carbon numbers of eight or more paraffin, polyolefine, etc. are desirable, for example, can use polyethylene, polypropylene, paraffin wax, a paraffin latex, a micro crystallin wax, carnauba wax, etc. As for the loadings of such polyolefines, it is desirable that it is generally 1 - 10% of the weight of the range.

[0083] As a coloring agent, the suitable pigment and suitable color of arbitration can be used if needed. For example, carbon black, chromium yellow, the aniline bule, a copper phthalocyanine blue, ultramarine blue, Quinacridone, benzidine yellow, etc. can be used.

[0084] As an electric charge control agent, azine system colors, such as a metallic complex of a fluorochemical surfactant, an azo system metallic complex, a salicylic-acid chromium complex, a dialkyl salicylic acid, and a naphthoic acid and Nigrosine, quarternary ammonium salt, carbon black, etc. can be used.

[0085] Moreover, as other additives, as an abrasive material, the tin oxide, strontium titanate, barium titanate, the tungsten carbide, etc. can be used, and the resin particle and non-subtlety particle which commit an electrification adjuvant, a conductive grant agent, a caking inhibitor, a fluid grant agent, etc. may be added.

[0086] As an approach of creating the magnetic toner concerning this invention It can carry out by the well-known approach by mixing, kneading, and grinding. Specifically Said magnetic-oxide-of-iron particle powder for magnetic toners and said binding resin, and the need are accepted. A coloring agent, After fully mixing first a release agent, an electric charge control agent, other additives, etc. with a mixer, With a heating kneading machine, grinding and a classification can be performed about the resin kneading object which was made to distribute a magnetic-oxide-of-iron particle etc. in [which were made to knead and compatibility-ize] melting, and was obtained after cooling solidification in resin etc., and a magnetic toner can be obtained.

[0087] Mixers, such as a Henschel mixer and a ball mill, can be used as said mixer. As said heating kneading machine, heating kneading machines, such as a roll mill, a kneader, a 2 shaft screw mold, and an extruder, can be used. Grinders, such as a cutter mill and a jet mill, can perform said grinding, and said classification can also be performed by the well-known approach.

[0088] As other methods of obtaining the magnetic toner concerning this invention, there is a suspension-polymerization method or an emulsion-polymerization method, and it sets by the suspension-polymerization method. A polymerization nature monomer and the magnetic-oxide-of-iron particle powder for magnetic toners, a coloring agent, and the need are accepted. A polymerization initiator, Stirring the monomer constituent which dissolves or distributed a cross linking agent, an electric charge control agent, and other additives in the aqueous phase containing a suspension stabilizer, it can add, a polymerization can be corned and carried out and a toner particle can be formed.

[0089] In an emulsion-polymerization method, the toner particle of a moderate grain size can be formed by adding an emulsifier in the process in which make a monomer, the magnetic-oxide-of-iron particle powder for magnetic toners, a coloring agent, a polymerization initiator, etc. distribute underwater, and a polymerization is performed.

[0090]

[Embodiment of the Invention] The gestalt of typical operation of this invention is as follows.

[0091] The mean particle diameter of magnetic-oxide-of-iron particle powder is the average of the numeric value measured from the electron microscope photograph, and the value measured with the BET adsorption method showed specific surface area. "Oscillating sample mold magnetometer VSM-

3S-15" (Toei Industry make) was used for magnetic properties, and they measured it to external magnetic field 10KOe, having applied it.
[0092] The particle shape of magnetic-oxide-of-iron particle powder was observed with the scanning electron microscope (Hitachi S-800). Moreover, what fulfills the following conditions about the projection in the particle front face of a magnetic-oxide-of-iron particle was authorized as a convex projection. That is, both the both ends of (1) projection should be concaves on the projection drawing (transmission electron microscope photograph) of a magnetic-oxide-of-iron particle.
(2) When two or more steps of projection parts have lapped, let only a part for the point be a projection.
(3) Satisfy the following type about the die length (a) of the base of a projection, height (b), and the particle diameter (c) of the particle concerned.
i) 10 <=a/cx100 <=40ii5 <=b/cx100 <=30[0093] The above (1) and (2) are judged by viewing on said projection drawing (transmission electron microscope photograph). It judged whether a/c and b/c would be computed by measuring [each / of the projection which is about the above (3) on the particle front face of the magnetic-oxide-of-iron particle in said projection drawing (transmission electron microscope photograph)] with a digitizer (H.P.-85B (product made from Hewlett Packard)) about the die length (a) of a base, height (b), and the particle diameter (c) of the particle concerned, and Conditions i and ii would be suited.
[0094] It judges whether it is the magnetic-oxide-of-iron particle which starts this invention by whether the convex projection with which it is satisfied of said conditions (1) thru/or (3) in said projection drawing is shown in a particle front face in 2-30 range. Furthermore, it judged whether it was the magnetic-oxide-of-iron particle powder for magnetic toners which the number of the particles which have a convex projection on the front face of a particle in 2-30 range all over said projection drawing computes the rate of occupying to a total particle number, and requires it for this invention.
[0095] the amount of Si of the magnetic-oxide-of-iron particle before surface treatment -- "an X-ray fluorescence equipment 3063M mold" (Rigaku Industrial Corp. make) -- using it -- JIS The value measured according to the "X-ray-fluorescence-analysis general notices" of K0119 showed. About the amount of Si on the front face of a particle before surface treatment, it measured by the following approach. Namely, after mixing the magnetic-oxide-of-iron particle powder and ion exchange water before surface treatment, After mixing with a hydroxylation alkali water solution and stirring what was made to distribute and was made into suspension more than for 30 minutes, The amount of Si of the magnetic-oxide-of-iron particle powder obtained by filtering suspension and drying was measured, and it considered as the amount of Si on the front face of a particle of the magnetic-oxide-of-iron particle before surface treatment with the difference with the total amount of Si before processing by said alkali.
[0096] The value calculated with the following method of chemical analysis showed the Fe2+ content. That is, in the bottom of an inert gas ambient atmosphere, 25 cc of mixed solutions which contain a phosphoric acid and a sulfuric acid at a rate of 2:1 to 0.5g of magnetic-oxide-of-iron particle powder is added, and the above-mentioned magnetic-oxide-of-iron particle is dissolved. After adding several drops of diphenylamine sulfonic acids to the diluent of this dissolution water solution as an indicator, oxidation reduction titration using a potassium-dichromate water solution was performed. The time of the above-mentioned diluent presenting purple was made into the terminal point, and it calculated and asked from the amount of the potassium-dichromate water solution used by the time it reached this terminal point.
[0097] About aluminum, Ti, Mg, Si, Co, Zr, Mn, and the amount of Zn which were made to put on a particle front face by surface treatment Each is measured by performing X-ray fluorescence according to the "X-ray-fluorescence-analysis general notices" of JIS-K -0119 using X-ray fluorescence equipment 3063M mold (Rigaku Industrial Corp. make). The amount of covering on the front face of a particle was computed by deducting the content of each element beforehand measured before covering. When the amount of covering was a minute amount, it measured using "inductively-coupled-plasma-atomic-emisson-spectroscopy equipment SPS 4000" (product made from SEIKO Electronic industry).
[0098] The value into which the hydrophobing processing agent presumed and converted the gestalt which exists in a particle front face from the carbon content measured using "being carbon sulfur

analysis apparatus EMIA-2200 among the Horiba metal" (Horiba Make) showed the amount of covering of a hydrophobing processing agent.
[0099] Using "amount measuring device TB-of blowing off electrifications 200" (Toshiba Chemical CORP. make), the amount of electrifications of magnetic-oxide-of-iron particle powder mixed magnetic-oxide-of-iron particle powder by 5% of concentration using TFV-200 / 300 (Powdertech make), and after the carrier performed shaking for 30 minutes, it measured it.
[0100] The condensation of magnetic-oxide-of-iron particle powder measured an umbrella consistency (rhoa) and tap density (rhot), respectively, and showed them with the value computed by having assigned them to the following type.
A fluidity becomes what was more excellent, so that condensation =[(rhot-rhoa) /rhot] x100, in addition condensation become small.
[0101] An umbrella consistency (rhoa) is measured by the pigment examining method of JIS-5101. In addition, tap density (rhot) You use a funnel and make it calmly filled up with 10g of magnetic-oxide-of-iron particle powder after umbrella density measurement into a 20 cc measuring cylinder. Subsequently The amount (cc) of the magnetic-oxide-of-iron particle powder with which it is filled up after repeating the actuation which carries out natural fall from height of 25mm 600 times was read in the graduation of a measuring cylinder, and the value computed by having assigned it to the following type showed.
Tap density (g/cc) = 10(g) / capacity (cc)
[0102] The oil absorption of magnetic-oxide-of-iron particle powder was measured by the pigment examining method of JIS-K -5101.
[0103] The exoergic initiation temperature (degree C) by the differential thermal analysis measured using "differential scanning calorimeter DSC-200" (product made from SEIKO Electronic industry) showed the thermal resistance of a magnetic-oxide-of-iron particle.
[0104] The volume mean diameter of a toner is Coulter. Counter It measured using TA-II (Coulter Electronics Co.).
[0105] Evaluation about caducous [from the toner particle front face of magnetic-oxide-of-iron particle powder] was performed by the following technique. That is, the resin kneading object which kneads magnetic-oxide-of-iron particle powder and styrene acrylic resin, and is obtained was ground, resin kneading object particle powder was created, the amount of the fines of the magnetic-oxide-of-iron particle powder which is made to carry out shaking of this resin kneading object particle powder for 60 minutes with a paint shaker, and is produced was observed with the electron microscope, and the comparison with the case where the conventional spherical magnetite-particles powder is used estimated.
[0106] 21.0l. of ferrous-sulfate water solutions containing <generation of magnetic-oxide-of-iron particle powder> Fe2+1.6 mol/l It adds to 20.7l. of 3.1-N sodium-hydroxide water solutions beforehand prepared into the reactor (it corresponds to 0.95Eq to Fe2+.). After generating ferrous-salt suspension which contains ferrous hydroxide salt colloid in pH6.7 and the temperature of 90 degrees C, Aeration of the air 80l./m is carried out, a first stage reaction is started, and it is 196.3g (SiO228.8wt%) (it corresponds to 4.5 atom % by Si conversion to Fe.) of No. 3 water glass as a silicon component to coincidence. What diluted with water and was set to 0.3l. was made dropped at the rate of 5ml/m. Oxidation reaction was continued after dropping termination of the above-mentioned water glass solution, stirring for 30 minutes, and the first iron suspension which is made to end a first stage reaction and contains a magnetite nucleus crystallite child was obtained. At this time, after oxidation reaction initiation, after whenever [oxidation / of Fe2+] exceeded 20%, pH was within the limits of 7.5-9.5, and moreover, after exceeding 30%, pH was within the limits of 8.0-9.5.
[0107] After adding 0.4l. of 9-N sodium-hydroxide water solutions to ferrous-salt suspension including the above-mentioned magnetite nucleus crystallite child after first stage reaction termination and adjusting pH of suspension to 9.5, in the temperature of 90 degrees C, aeration of the air 100l./m was carried out for 30 minutes, the second stage reaction was performed, and magnetite particles were made to generate. The generation particle was dried and ground the rinsing and ** exception with the

conventional method.
[0108] The particle shape had the shape of konpeito with the round angle based on the shape of a grain the passage clear from the transmission electron microscope photograph (x50000) shown in drawing 1 , and the obtained magnetite particles had a regular grain size, and mean particle diameter was [the values of 0.20 micrometers and a BET specific surface area] 10.4m2 / g.
[0109] As a result of inspecting [projection / on the front face of a particle] about said inspection approach (1) about a convex projection thru/or (3), the particle which has 2-30 convex projections per one particle was several 76% to the total particle number.
[0110] Moreover, this magnetite-particles powder did 3.7 atom % content of Si to Fe as a result of X-ray fluorescence, and the amount of Si on the front face of a particle was 0.19 atoms %. Moreover, as a result of oxidation reduction titration, the amount of Fe2+ was 18.4 % of the weight, and was what has whenever [sufficient / black]. The saturation magnetization values of magnetic properties were 88.7 emu/g. It was what is excellent in a fluidity from the measurement result of condensation. The amount of electrifications was -18.0microC/g. Oil absorption was 20ml / 100g, and exoergic initiation temperature was 131 degrees C.
[0111] As a result of creating the resin kneading object particle powder which is the grinding object of the resin kneading object which kneads said magnetite-particles powder and styrene acrylic resin which were obtained, and is obtained and said evaluation approach's estimating caducous [of magnetic-oxide-of-iron particle powder], it was what has sufficient omission prevention effectiveness.
[0112] <Covering processing> After making 80-degree C water distribute 1kg of said magnetite-particles powder, stirring, the sodium-hydroxide water solution was dropped and pH was set to 11. Next, the water solution which contains 12.7g of 0.20% of the weight of aluminum sulfates by aluminum conversion to this particle was dropped, the 3.6-N sulfuric acid was dropped, and pH was adjusted to 5 and stirred for 5 minutes. Then, the sodium-hydroxide water solution was dropped, and it adjusted to pH7, and stirred for 30 minutes. Then, after filtering and rinsing, it dried at 60 degrees C and the magnetite-particles powder which the hydroxide of aluminum has put on the particle front face was obtained.
[0113] The BET specific surface area was [10.6m2 / g, and the saturation magnetization of aluminum content on 88.2 emu/g and the front face of a particle] 0.18 % of the weight, and oil absorption was [20ml / 100ml, and the exoergic initiation temperature of the magnetite-particles powder which the hydroxide of aluminum has put on said obtained particle front face] 158 degrees C.
[0114] The magnetite-particles powder which the hydroxide of aluminum has put on said obtained particle front face was what has sufficient omission prevention effectiveness, as a result of maintaining the particle shape of the shape of konpeito with the round angle based on the shape of a grain before covering and said evaluation approach's estimating caducous [of the magnetic-oxide-of-iron particle powder from resin kneading object particle powder]. Moreover, it was what maintains the property excellent also in the fluidity.
[0115]
<Manufacture of a magnetic toner> Styrene-n-butyl acrylate copolymer The 100 weight sections (250,000 copolymerization ratio = 85:15 Mw = Tg= 62 degrees C)
magnetic-oxide-of-iron particle powder (thing of the gestalt of operation of this invention) 80 weight sections Forward electric charge control agent The 1.5 weight sections Low-molecular-weight ethylene propylene rubber 2 roll mills set as 140 degrees C in the 2 weight sections above-mentioned mixture -- heat kneading during about 15 minutes -- carrying out -- after cooling and coarse grinding -- it pulverized. Furthermore, fines and coarse powder were cut for this by the classification, and the magnetic toner with a volume mean diameter of 10.4 micrometers was obtained.
[0116] Adjust the one component system developer which consists of an obtained magnetic toner, and by the durability test by shaking trial according to a paint shaker about fogging according to image concentration about an image When generating of the fines of the magnetic-oxide-of-iron particle from a magnetic toner was investigated, compared with the case where the 1 component developer which consists of a magnetic toner which used the conventional spherical magnetic-oxide-of-iron particle

powder is used, it was the image quality of high resolution, and the endurance as which generating of fines is moreover hardly regarded was good.
[0117]
[Function] Surface treatment has been performed in order to make it bind more firmly [in order to control the pulverization by the magnetic particle powder from a toner particle front face being omitted conventionally] about association with the particle front face of said magnetic particle, and resin. However, when the point of the binding property of a particle front face and resin is considered, making [more] a touch area considers that this invention person will be effective about the point of the omission prevention from a toner front face, and as a result of examining wholeheartedly the point whether the thing of the configuration which is irregular about the configuration of a magnetic particle is obtained, he results in this invention.
[0118] In the manufacturing method of the magnetite-particles powder with which this invention person consists of two staircase reactions [whether during a first stage reaction, to Fe, the water-soluble silicate water solution of 1.0 - 8.0 atom % is divided into at least 2 times or more, and it adds by Si conversion, and] Or it is dropped to the Si total addition at the rate of per minute 0.5 - 5.0% of range. And the magnetite particles of the shape of konpeito with the angle round when whenever [oxidation / of Fe2+ under said first stage reaction] (Fe3+ / total Fe) makes pH the range of 7.5-9.5 in 20% or more of range based on the shape of a grain are obtained. From there being no omission from a toner front face, and excelling in endurance, when it considers as a toner, and containing Si on a particle front face Since electrification nature with it is obtained, it finds out that the magnetic-oxide-of-iron particle powder for magnetic toners with which the image quality of high resolution is acquired in electrostatic latent-image development is obtained. [the good fluidity when considering as a toner and] [uniform]
[0119] In addition, the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which made either the oxide of a specific element, a hydroxide, water oxides or such mixture put on a particle front face 60% or more at a number rate should be excelled in thermal resistance.
[0120] Moreover, oil absorption of the magnetic-oxide-of-iron particle powder for magnetic toners which contains the magnetic-oxide-of-iron particle which made the hydrophobing processing agent put on a particle front face 60% or more at a number rate can be lessened, and the dispersibility to resin can be improved.
[0121]
[Example] Next, the example of a comparison is given in an example list.
[0122] Examples 1-22, examples 1-11 of a comparison;
21.0l. of ferrous-sulfate water solutions containing <manufacture of magnetic-oxide-of-iron particle powder> example 1Fe2+1.6 mol/l It adds to 20.7l. of 3.1-N sodium-hydroxide water solutions beforehand prepared into the reactor (it corresponds to 0.95Eq to Fe2+.). After generating ferrous-salt suspension which contains ferrous hydroxide salt colloid in pH6.7 and the temperature of 90 degrees C, Aeration of the air 80l./m is carried out, a first stage reaction is started, and it is 196.3g (SiO228.8wt%) (it corresponds to 4.5 atom % by Si conversion to Fe.) of No. 3 water glass as a silicon component to coincidence. What diluted with water and was set to 0.3l. was divided into 0.06l. 5 times every [each] 10 minutes, and it added. Oxidation reaction was continued after dropping termination of the above-mentioned water glass solution, stirring for 30 minutes, and the first iron suspension which is made to end a first stage reaction and contains a magnetite nucleus crystallite child was obtained. At this time, after oxidation reaction initiation, after whenever [oxidation / of Fe2+] exceeded 20%, pH was within the limits of 7.5-9.5, and moreover, after exceeding 30%, pH was within the limits of 8.0-9.5.
[0123] After adding 0.4l. of 9-N sodium-hydroxide water solutions to ferrous-salt suspension including the above-mentioned magnetite nucleus crystallite child after first stage reaction termination and adjusting pH of suspension to 9.5, in the temperature of 90 degrees C, aeration of the air 100l./m was carried out for 30 minutes, the second stage reaction was performed, and magnetite particles were made to generate. The generation particle was dried and ground the rinsing and ** exception with the conventional method.

[0124] The particle shape had the shape of konpeito with the round angle based on the shape of a grain, and the obtained magnetite particles had a regular grain size, and mean particle diameter was [the values of 0.19 micrometers and a BET specific surface area] 11.3m2 / g.
[0125] As a result of inspecting [projection / on the front face of a particle] about said inspection approach (1) about a convex projection thru/or (3), the particle which has 2-30 convex projections per one particle was several 81% to the total particle number.
[0126] Moreover, this magnetite-particles powder did 3.7 atom % content of Si to Fe as a result of X-ray fluorescence, and the amount of Si on the front face of a particle was 0.21 atoms %. Moreover, as a result of oxidation reduction titration, the amount of Fe2+ was 18.2 % of the weight, and was what has whenever [sufficient / black]. The saturation magnetization values of magnetic properties were 88.0 emu/g. It was what is excellent in a fluidity from the measurement result of condensation. The amount of electrifications was -20.0microC/g. Oil absorption was 21ml / 100g, and exoergic initiation temperature was 134 degrees C.
[0127] As a result of creating the resin kneading object particle powder which is the grinding object of the resin kneading object which kneads said magnetite-particles powder and styrene acrylic resin which were obtained, and is obtained and said evaluation approach's estimating caducous [of magnetic-oxide-of-iron particle powder], it was what has sufficient omission prevention effectiveness.
[0128] Magnetite-particles powder was obtained like the gestalt of operation of this invention, or the example 1 except having changed various reaction temperature in a second stage reaction in the class list [in / to the class of ferrous-salt water solution in examples 2-3, the example 1 of a comparison - 7 first stage reactions, and a concentration list / the class list of the amount used and a hydroxylation alkali water solution] of a hydroxylation alkali water solution [in / to concentration and the addition approach list of water glass / Adjustment pH and the second stage reaction under an addition and first stage reaction]. Many properties of the magnetic-oxide-of-iron particle powder obtained in Table 1 in the main manufacture conditions at this time are shown in Table 2.
[0129]
[Table 1]

[0130]

実施例及び比較例	磁性酸化鉄粒子粉末の製造条件												
	第一段反応										第二段反応		
	第一鉄塩溶液	水酸化アルカリ	当量比 20H/Fe	Si添加				pH調整		反応温度	水酸化アルカリ	当量比 残存Fe^{2+}対比	反応温度
				水可溶性ケイ酸塩	Si添加量 Si/Fe (atom%)	添加時期	添加方法	pH範囲	pH調整時期 酸化度 (%)	(℃)		20H/Fe	(℃)
実施例1	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	反応開始時～10分毎に	5分割添加	8.0 ～9.5	30%以降	90	水酸化ナトリウム	1.1	90
実施例2	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	3.0	反応開始時～5%/minで	連続滴下	8.0 ～9.5	30%以降	95	水酸化ナトリウム	1.1	95
実施例3	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	6.0	反応開始時～5%/minで	連続滴下	8.0 ～9.5	30%以降	85	水酸化ナトリウム	1.1	85
比較例1	硫酸第一鉄	水酸化ナトリウム	0.99	3号水ガラス	0.3	反応開始時～5%/minで	連続滴下	8.0 ～9.5	30%以降	90	水酸化ナトリウム	1.1	90
比較例2	硫酸第一鉄	水酸化ナトリウム	0.90	3号水ガラス	9.0	反応開始時～5%/minで	連続滴下	8.0 ～9.5	30%以降	90	水酸化ナトリウム	1.1	90
比較例3	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	反応開始直後	一括投入	8.0 ～9.5	30%以降	90	水酸化ナトリウム	1.1	90
比較例4	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	反応開始時～5%/minで	連続滴下	6.7 ～7.5	30%以降	90	水酸化ナトリウム	1.1	90
比較例5	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	反応開始時～5%/minで	連続滴下	9.5 ～10.0	30%以降	90	水酸化ナトリウム	1.1	90
比較例6	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	反応開始時～5%/minで	連続滴下	8.0 ～9.5	5%以降	90	水酸化ナトリウム	1.1	90
比較例7	硫酸第一鉄	水酸化ナトリウム	0.95	3号水ガラス	4.5	仕込投入時	一括投入	8.0 ～9.5	30%以降	90	水酸化ナトリウム	1.1	90

[Table 2]

[0131] The magnetite-particles powder obtained in the example 1 of a comparison does not have the hexahedron configuration a passage clear from the electron microscope photograph (x50000) shown in drawing 3 , and since there is little Si which the omission prevention effectiveness from a resin kneading object particle front face is not enough, and is contained on a particle front face compared with the magnetite-particles powder of an example 1, it is inferior to a fluidity.
[0132] After making 80-degree C water distribute 1kg of magnetite-particles powder obtained in the <covering processing> example 4 example 1, stirring, the sodium-hydroxide water solution was dropped and pH was set to 11. Next, after the water solution which contains 63.4g of 1.00% of the weight of aluminum sulfates by aluminum conversion to this particle was dropped and the 3.6-N sulfuric acid was dropped, it adjusted to pH7 and stirred for 30 minutes. Then, after filtering and rinsing, it dried at 60 degrees C and the magnetite-particles powder which the hydroxide of aluminum has put on the particle front face was obtained.
[0133] Covering processing was performed like the example 4 except having changed various class of examples 5-8, the example 8 of a comparison - 9 processed particle, and processing object, and its addition. The conditions of covering processing and many acquired properties of magnetic-oxide-of-iron particle powder were shown in Table 3.
[0134]
[Table 3]

実施例及び比較例	金属酸化物又は金属含水酸化物による被着処理				被着処理したマグネタイト粒子粉末の諸特性						
	被処理粒子粉末		処理物		平均粒径	BET 比表面積	Si含有量	飽和磁化	被着物の被着量	吸油量	発熱開始温度
	種類	発熱開始温度℃	種類	添加量 (wt%)	(μm)	(m^2/g)	Si/Fe (atom%)	(emu/g)	(wt%)	ml/100g	(℃)
実施例4	実施例1の表面処理前マグネタイト粒子粉末	134	硫酸アルミニウム	Al 1.0	0.19	12.0	3.7	87.0	Al 0.89	21	221
実施例5	実施例1の表面処理前マグネタイト粒子粉末	134	硫酸アルミニウム	Al 2.5	0.20	12.4	3.6	85.4	Al 2.1	22	287
実施例6	実施例2の表面処理前マグネタイト粒子粉末	127	硫酸チタニル	Ti 1.5	0.20	10.5	1.2	87.5	Ti 1.37	20	245
実施例7	実施例3の表面処理前マグネタイト粒子粉末	158	硫酸チタニル	Ti 1.0	0.18	16.8	5.3	86.3	Ti 0.92	23	252
実施例8	実施例1の表面処理前マグネタイト粒子粉末	134	硫酸マグネシウム	Mg 0.20	0.19	11.6	3.7	86.9	Mg 0.17	21	154
比較例8	実施例1の表面処理前マグネタイト粒子粉末	134	硫酸アルミニウム	Al 0.03	0.19	11.2	3.7	87.8	Al 0.02	21	138
比較例9	実施例1の表面処理前マグネタイト粒子粉末	134	硫酸アルミニウム	Al 20.0	0.22	25.6	3.2	72.6	Al 18.2	25	312

[0135] The magnetite-particles powder which the silane coupling agent has put on the particle front face was obtained by supplying 10kg of magnetite-particles powder obtained with the gestalt of the <hydrophobing processing> example 9 aforementioned implementation, and silane coupling agent A-143 (Nippon Unicar make) 15g to a wheel mold kneading machine (trade name: made in sand mill

Matsumoto casting iron works), and operating it for 1 hour.
[0136] Hydrophobing processing was performed like the example 9 except having changed various class of examples 10-15, the example 10 of a comparison - 11 processed particle, and hydrophobing processing agent, and its addition. The conditions of hydrophobing processing and many acquired properties of magnetic-oxide-of-iron particle powder were shown in Table 4. In addition, as hydrophobing processing agents other than the above, it is a titanate coupling agent. The BUREN act TTS (Ajinomoto Co., Inc. make) and the iso palmitic acid (product made from Nissan Chemistry) were used.
[0137]
[Table 4]

実施例及び比較例	疎水化処理				疎水化処理したマグネタイト粒子粉末						
	被処理粒子粉末		疎水化処理剤		平均粒径	BET 比表面積	Si含有量	飽和磁化	疎水化剤被膜量		吸油量
	種類	吸油量 ml/100g	種類	添加量 (wt%)	(μm)	(m^2/g)	Si/Fe (atom%)	(emu/g)	炭素量 (wt%)	被膜換算量 (wt%)	ml/100g
実施例9	実施の形態の表面処理前マグネタイト粒子粉末	20	シランカップリング剤 A-143	0.20	0.20	10.2	3.7	88.3	0.04	0.12	18
実施例10	実施例1の表面処理前マグネタイト粒子粉末	21	シランカップリング剤 A-143	2.5	0.19	10.0	4.0	86.4	0.45	1.32	17
実施例11	実施例2の表面処理前マグネタイト粒子粉末	18	シランカップリング剤 A-143	4.0	0.20	7.9	1.7	86.8	0.72	2.11	14
実施例12	実施例1の表面処理前マグネタイト粒子粉末	21	チタネートカップリング剤プレンアクトTTS	2.0	0.19	9.2	3.6	85.9	1.36	1.88	17
実施例13	実施例2の表面処理前マグネタイト粒子粉末	18	チタネートカップリング剤プレンアクトTTS	4.5	0.20	7.2	1.2	84.8	3.05	4.22	14
実施例14	実施例3の表面処理前マグネタイト粒子粉末	22	イソパルミチン酸 日産化学	0.15	0.18	15.6	5.3	85.1	0.11	0.14	20
実施例15	実施の形態の表面処理前マグネタイト粒子粉末	20	イソパルミチン酸 日産化学	2.5	0.20	7.8	3.6	86.2	1.88	2.34	16
比較例10	実施例1の表面処理前マグネタイト粒子粉末	21	シランカップリング剤 A-143	0.05	0.19	11.4	3.7	87.8	0.01	0.03	21
比較例11	実施例1の表面処理前マグネタイト粒子粉末	21	チタネートカップリング剤プレンアクトTTS	15.0	0.19	6.3	3.3	76.2	10.17	14.08	13

[0138] The magnetite-particles powder which the silane coupling agent has put on the particle front face was further obtained by supplying 10kg of magnetite-particles powder which the hydroxide of aluminum has put on the particle front face obtained with the gestalt of the <covering processing and hydrophobing processing> example 16 aforementioned implementation, and silane coupling agent A-143 (Nippon Unicar make) 20g to a wheel mold kneading machine (trade name: made in sand mill Matsumoto casting iron works), and operating it for 1 hour.
[0139] Hydrophobing processing was performed like the example 16 except having changed various the class of processed particle which the oxide of a specific element etc. has put on the example 17 - 22 particle front face, class of hydrophobing processing agent, and its addition. The conditions of hydrophobing processing and many acquired properties of magnetic-oxide-of-iron particle powder were shown in Table 5.
[0140]
[Table 5]

実施例及び比較例	疎水化処理					疎水化処理したマグネタイト粒子粉末							
	被処理粒子粉末			処理剤		平均粒径	BET 比表面積	Si含有量	飽和磁化	疎水化剤被着量		吸油量	発熱開始温度
	種類	吸油量 ml/100g	発熱開始温度 (℃)	種類	添加量 (wt%)	(μm)	(m^2/g)	Si/Fe (atom%)	(emu/g)	炭素量 (wt%)	乾燥後減量 (wt%)	ml/100g	(℃)
実施例16	実施の形態の被着処理後マグネタイト粒子粉末	20	158	シランカップリング剤 A-143	0.2	0.20	10.4	3.7	87.6	0.04	0.12	18	170
実施例17	実施の形態の被着処理後マグネタイト粒子粉末	20	158	シランカップリング剤 A-143	3.5	0.20	9.2	4.1	86.3	0.63	1.85	15	211
実施例18	実施例4の被着処理後マグネタイト粒子粉末	21	221	シランカップリング剤 A-143	3.0	0.19	10.2	4.0	85.2	0.54	1.58	16	258
実施例19	実施の形態の被着処理後マグネタイト粒子粉末	20	158	チタネートカップリング剤 プレンアクトTTS	2.0	0.20	8.6	3.6	86.3	1.36	1.88	18	203
実施例20	実施例4の被着処理後マグネタイト粒子粉末	21	221	チタネートカップリング剤 プレンアクトTTS	2.5	0.19	9.8	3.6	84.2	1.70	2.35	17	286
実施例21	実施例6の被着処理後マグネタイト粒子粉末	20	245	シランカップリング剤 A-143	1.5	0.20	9.3	1.4	86.5	0.27	0.79	17	288
実施例22	実施例6の被着処理後マグネタイト粒子粉末	20	245	チタネートカップリング剤 プレンアクトTTS	3.0	0.20	7.7	1.2	84.5	2.03	2.81	16	294

[0141]
[Effect of the Invention] The magnetic-oxide-of-iron particle powder for magnetic toners concerning this invention Grain size is the very fine particle which is 0.05-0.50 micrometers, and particle shape has the shape of konpeito with the round angle based on the shape of a grain. and the magnetic-oxide-of-iron particle whose number of the convex projections on a particle front face is 2-30 range from containing 60% or more at a number rate on projection drawing From there being no omission from a toner particle and containing many Si on a particle front face Are the optimal as magnetic-oxide-of-iron particle powder for magnetic toners with which the image quality of high resolution is acquired in electrostatic latent-image development since electrification nature with it is obtained. [the good fluidity when making it a toner and] [uniform] Furthermore, when exoergic initiation temperature is as high as 150 degrees C or more, it can be stabilized and used also in use in a high temperature requirement, and it is

enough, and the hydrophobicity on the front face of a particle can make dispersibility to resin good, when there is little oil absorption.

[Translation done.]